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(54) [Title of the Invention] **Radiation-curable Adhesive, Polyester Film-Laminated Metal Sheet Using Same, and Production Thereof**

(57) [Abstract]

[Object]To provide a radiation-curable adhesive with improved properties such as better adhesion between polyester film and metal materials, as well as better retort properties when used on food product cans; polyester film-laminated metal sheets using such an adhesive; and a method for producing such metal sheets.

[Structure] A radiation-curable adhesive, comprising 2 to 200 weight parts polyester or polyurethane oligomer with unsaturated double bonds per 100 weight parts polyester resin; the adhesive is used to laminate a polyester film to a metal material, and the two materials are heated and are cured by radiation.

[Claims]

[Claim 1] A radiation-curable adhesive, comprising 2 to 200 weight parts (solids) of a polyester oligomer and/or polyurethane oligomer with 0.3 to 5.0 mol/kg molecule polymerizable unsaturated double bonds and a number average molecular weight of 300 to 5,000 per 100 weight parts polyester resin (solids) with a number average molecular weight of 7,000 to 40,000.

[Claim 2] A polyester film-laminated metal sheet, comprising a metal material laminated with a polyester film using a radiation-curable adhesive itself comprising 2 to 200 weight parts (solids) of a polyester oligomer and/or polyurethane oligomer with 0.3 to 5.0 mol/kg molecule polymerizable unsaturated double bonds and a number average molecular weight of 300 to 5,000 per 100 weight parts polyester resin (solids) with a number average molecular weight of 7,000 to 40,000, the laminated materials being heated and cured by radiation.

[Claim 3] A method for producing a polyester film-laminated metal sheet, characterized in that a metal material is laminated with a polyester film using a radiation-curable adhesive itself comprising 2 to 200 weight parts (solids) of a polyester oligomer and/or polyurethane oligomer with 0.3 to 5.0 mol/kg molecule polymerizable unsaturated double bonds and a number average molecular weight of 300 to 5,000 per 100 weight parts polyester resin (solids) with a number average molecular weight of 7,000 to 40,000; the adhesive is then heated for a short period of time to a temperature no greater than the softening point of the polyester film; and the adhesive is then cured by the irradiation of electron beams through the film layer.

[Detailed Description of the Invention]

[0001]

[Field of Industrial Application]

The present invention relates to a radiation-curable adhesive, a polyester film-laminated metal sheet using such an adhesive; and a method for producing such a laminated metal sheet.

[0002]

[Prior Art]

Conventional polyester film-laminated metal sheets which have been used for beverage cans and food product cans (referred to below as PET laminated metal sheets) are usually produced by laminating a polyester film and a metal sheet using an adhesive (such as described in JP-A 3-87249).

[0003] Conventional methods for producing PET laminated metal sheets comprise the steps of (1) applying an adhesive to a polyester film (referred to below as PET film) and drying the adhesive until it is tack-free (usually a few seconds at around 100°C), (2) laminating the adhesive-coated PET film with a metal sheet by heating them (usually 0.5 second at around 180°C, and (3) post-baking the adhesive (usually 60 to 100 seconds at around 180°C) to complete the curing process. Because of recent growing demand for mass production of PET laminated metal sheets, it has become necessary to make longer post-baking furnaces in order to permit more rapid production on high-speed production lines in the conventional method described above, which has resulted in the problems of greater costs associated with large-scale equipment, as well as the need for greater plant space.

[0004]

[Problems Which the Invention Is Intended to Solve]

In view of the foregoing, an object of the present invention is to develop a method of production suitable for high-speed production PET laminated metal sheets without the need for large-scale equipment and more space. Another object of the invention is to provide PET laminated metal sheets with better performance than conventional products, such as better adhesion between PET film and metal materials, as well as better retort properties when used for food product cans. Yet another object of the present invention is to provide a radiation-curable adhesive which is effective for the applications described above.

[0005]

[Means for Solving the Abovementioned Problems]

As a result of extensive research to overcome the problems described above, the inventors perfected the present invention when they noted that the first step (1) in conventional methods for producing PET laminated metal sheets requires heat to ensure that the solvent is evaporated off until the applied adhesive is tack-free, and that the second step (2) requires heat to soften the PET film and ensure the adhesion of the adhesive, but that the third step (3) is intended to improve the retort properties by ensuring the completion of the adhesive curing reaction and therefore does not necessarily require the use of heating means, it being possible to bring about a more rapid (in a few seconds) curing reaction by using a specific radiation-curable adhesive, which was found to give a PET laminated metal sheet with better adhesion, retort properties, and the like.

[0006] The present invention relates to:

"1. A radiation-curable adhesive, comprising 2 to 200 weight parts (solids) of a polyester oligomer and/or polyurethane oligomer with 0.3 to 5.0 mol/kg molecule polymerizable unsaturated double bonds and a number average molecular weight of 300 to 5,000 per 100 weight parts polyester resin (solids) with a number average molecular weight of 7,000 to 40,000;

"2. a polyester film-laminated metal sheet, comprising a metal material laminated with a polyester film using a radiation-curable adhesive itself comprising 2 to 200 weight parts (solids) of a polyester oligomer and/or polyurethane oligomer with 0.3 to 5.0 mol/kg molecule polymerizable unsaturated double bonds and a number average molecular weight of 300 to 5,000 per 100 weight parts polyester resin (solids) with a number average molecular weight of 7,000 to 40,000, the laminated materials being heated and cured by radiation; and

"3. a method for producing a polyester film-laminated metal sheet, characterized in that a metal material is laminated with a polyester film using a radiation-curable adhesive itself comprising 2 to 200 weight parts (solids) of a polyester oligomer and/or polyurethane oligomer with 0.3 to 5.0 mol/kg molecule polymerizable unsaturated double bonds and a number average molecular weight of 300 to 5,000 per 100 weight parts polyester resin (solids) with a number average molecular weight of 7,000 to 40,000; the adhesive is then heated for a short period of time to a temperature no greater than the softening point of the polyester film; and the adhesive is then cured by the irradiation of electron beams through the film layer."

[0007] The present invention is illustrated in greater detail below. The radiation-curable adhesive of the present invention comprises 2 to 200 weight parts of a polyester oligomer and/or polyurethane oligomer (occasionally referred to below simply as "oligomer") with 0.3 to 5.0 mol/kg molecule polymerizable unsaturated double bonds and a number average molecular weight of 300 to 5,000 per 100 weight parts polyester resin with a number average molecular weight of 7,000 to 40,000.

[0008] The polyester resin component must, first and foremost, be adhesive, since an object of the invention is to ensure adhesion between metal and PET film. It must also be flexible for when

the final product is processed. It must also be water-resistant, weather-resistant, chemical-resistant, and heat-resistant, while the adhesive layer formed on the laminated metal sheet must furthermore be durable.

[0009] The polyester resin used in the invention can be a conventional thermoplastic resin in the form of a polybasic acid and polyhydric alcohol condensate, where the number average molecular weight can range from 7,000 to 40,000, and preferably from 10,000 to 30,000.

[0010] Examples of polybasic acids include aliphatic dibasic acids such as adipic acid, suberic acid, azelaic acid, sebacic acid, and decane-1,10-dicarboxylic acid; alicyclic polybasic acids and anhydrides such as hexahydrophthalic acid, hexahydrotrimellitic acid, and tetrahydrophthalic acid; aromatic polybasic acids and anhydrides such as phthalic acid, isophthalic acid, terephthalic acid, trimellitic acid, and pyromellitic acid; and other acids such as maleic acid, fumaric acid, and itaconic acid.

[0011] Examples of polyhydric alcohols include ethylene glycol, propylene glycol, diethylene glycol, 1,2-butylene glycol, 1,6-hexanediol, 1,4-cyclohexanedimethanol, neopentyl glycol, and polylactone diol. The polyester resin can be produced by a common method, such as polycondensation of the aforementioned acid and alcohol components at a temperature of 200 to 250°C in a reaction vessel.

[0012] The oligomer component used in conjunction with the polyester resin comprises a polyester oligomer and/or polyurethane oligomer with a number average molecular weight of 300 to 5,000, and preferably 1,000 to 2,000, and 0.3 to 5.0 mol/kg molecule, and preferably 1.0 to 3.0 mol/kg molecule, polymerizable unsaturated double bonds.

[0013] Polyester oligomers comprise a (meth)acrylic acid bonded in the form of an ester to a low molecular weight hydroxylated polyester with a number average molecular weight of no more than 5,000. Low molecular weight polyesters can be obtained by condensation of the aforementioned polyhydric alcohols and polybasic acids serving as components of the polyester resin.

[0014] Polyurethane oligomers can be obtained by a reaction between a hydroxylated unsaturated monomer (such as 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, or allyl alcohol) and a polyisocyanate with at least two isocyanate groups per molecule or a urethane prepolymer with at least 2 isocyanate groups per molecule obtained by a reaction between a polyisocyanate such as that described above and a polyol with at least 2 hydroxyl groups per molecule.

[0015] Examples of polyisocyanates with at least 2, and preferably 2 to 3, isocyanate groups per molecule include aliphatic, alicyclic, aromatic, and aromatic-aliphatic types of polyisocyanate, such as tolylene diisocyanate, 4,4'-diphenylmethane diisocyanate, xylylene diisocyanate, hexamethylene diisocyanate, lysine diisocyanate, and 1,6-hexane diisocyanate.

[0016] Examples of polyols with at least 2 hydroxyl groups per molecule (which are used to obtain a urethane prepolymer) include ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, polyethylene glycol (those with a molecular weight of no more than 4,000), trimethylene glycol, polypropylene glycol (those with a molecular weight of no more than 4,000), tetramethylene glycol, polytetramethylene glycol (those with a molecular weight of no more than 4,000), 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 1,3-pentanediol, neopentyl glycol, 1,2-hexylene glycol, and 1,6-hexanediol.

[0017] Polyester resins with a number average molecular weight lower than 7,000 tend to have poor corrosion resistance and water resistance. More than 40,000, on the other hand, will not give a high solid adhesive.

[0018] Oligomers with a number average molecular weight lower than 300 will not allow the adhesive layer to become tack-free before prior to hot lamination. More than 5,000, on the other hand, will result in less curing when irradiated.

[0019] The oligomer is blended in a proportion of 2 to 200 weight parts, preferably 5 to 100 weight parts, and even more preferably 10 to 50 weight parts, per 100 weight parts polyester resin. Less than 2 weight parts will not produce satisfactory radiation curing properties or performance such as retort resistance. More than 200 weight parts, on the other hand, will not allow the adhesive layer to become tack-free prior to hot lamination, and will also result in poor

thermal stability when the PET laminated metal sheet is heat-treated after the radiation curing process.

[0020] The radiation-curable adhesive of the present invention is obtained by mixing the polyester resin and oligomer components, which are then diluted with an organic solvent such as methyl ethyl ketone or toluene. The adhesive may also be colored with the addition of a pigment such as titanium oxide.

[0021] In the present invention, ethylene terephthalate units constitute between 75 and 100% of the ester repeating units of the PET film which is to be laminated with the metal material using the radiation-curable adhesive. The ester units other than the ethylene terephthalate units may include ester units such as of phthalic acid, isophthalic acid, succinic acid, and adipic acid. The surface of the PET film may be treated by corona discharge or the like to enhance the adhesion with the adhesive.

[0022] Metal sheets which can be used include hot-rolled, cold-rolled, galvanized, and zinc alloy-plated copper sheets, electrogalvanized and zinc alloy-plated steel sheets, tin plate, tin-free steel, aluminum-plated steel sheets, terneplate steel sheets, nickel-plated steel sheets and other types of alloy-plated steel sheets, stainless steel, aluminum sheets, copper sheets, titanium sheets, and other alloy sheets, as well as any of the above which have undergone conversion treatment as needed, such as phosphate treatment, chromate treatment, organic chromate treatment, cobalt complex oxide film treatment, nickel substitute plating treatment, or some other treatment.

[0023] The method for producing the PET laminated metal sheet is described below. A 5 to 30 μm thick PET film is first coated with the adhesive using a roll coater, gravure method, gravure offset method, sprayer, or some other common means of application to a dry film thickness of 1 to 5 μm, and it is dried as needed for a few seconds at a temperature around 100°C until it is tack-free. The metal material is then placed on the adhesive layer and is hot laminated for no more than 2 seconds at a temperature no greater than the softening point of the PET film (about 230°C or lower).

[0024] The resulting laminated metal sheet is then irradiated with electron beams through the PET film. The accelerator for the radiation source used in the irradiation can be a Cockcroft type,

Cockcroft-Walton type, Van der Graft type, resonance transformer type, transformer type, insulated core transformer type, dynamitron type, linear filament type, area beam type, or high frequency type. Radiation equal to 100 KeV to 300 KeV, and preferably 150 KeV to 200 KeV, is needed to cure and dry the radiation-curable adhesive in the present invention. A radiation dose of 0.2 Mrad to 15 Mrad is suitable, while 1 Mrad to 5 Mrad is more desirable. Less than 0.2 Mrad will not permit the adhesive to be fully cured, resulting in an adhesive layer with poor performance. More than 15 Mrad may compromise the mechanical strength of the PET film. The irradiation time is no more than about 1 second, about 1/100 of the time needed for conventional heated curing.

[0025]

[Examples] The invention is illustrated in the following examples.

Production of Polyester Resin

[0026] Production Example 1

18.3 weight parts dimethyl terephthalate, 11.7 weight parts dimethyl isophthalate, 11.9 weight parts ethylene glycol, 20.5 weight parts neopentyl glycol, 118 mg zinc acetate dihydrate as the ester interchange catalyst, and 246 mg antimony trioxide as the polycondensation catalyst were introduced into a 1 L autoclave. The contents were heated to between 160 and 210°C to bring about ester interchange, and the ester interchange reaction was concluded about 2 hours later when the stoichiometric amount of methanol was distilled off. A minute amount of trimethyl phosphate was added at this point, and the contents were stirred for 30 minutes at 200 to 210°C. The temperature was then increased to 220°C, 37.6 weight parts azelaic acid was added, and an ester interchange reaction was brought about for 30 minutes at between 220 and 230°C. The temperature was then increased to 250°C and the pressure was simultaneously reduced to get rid of the excess glycol at a temperature of 250°C and a pressure of 10 mmHg. The temperature was further increased and the pressure further reduced, giving a polyester resin (I) with a number average molecular weight of 30,000 and an OH value of 6.5. The resin (I) was diluted with methyl ketone/cyclohexanone (50/50) to a solids content of 30 wt%.

[0027] Production Example 2

A polyester resin (II) solution was synthesized with the following composition in the same manner as in Production Example 1.

dimethyl terephthalate	22.2 weight parts
dimethyl isophthalate	32.7 weight parts
sebacic acid	19.0 weight parts
ethylene glycol	10.1 weight parts
neopentyl glycol	26.2 weight parts

The resulting resin (II) had a number average molecular weight of 25,000.

[0028] Production of Polyester Oligomer

Production Example 3

1.0 trimethylol propane, 2.0 mol triethylene glycol, 1.0 mol 1,6-hexanediol, 3.0 mol adipic acid, and dibutyl tin oxide were blended in a catalytic amount to produce a polyester with a number average molecular weight of 850 and a hydroxyl group value of 200 in the conventional manner. The resulting polyester and acrylic acid were then blended in a proportion of 1.25 equivalents acrylic acid per 1.0 equivalent hydroxyl group of the polyester. 100 ppm polymerization inhibitor (hydroquinone) was added, a reaction was brought about at 80 to 100°C, and the reaction was stopped at a conversion of approximately 85 wt%, at which point the solvent and unreacted acrylic acid were distilled off, giving a polyester acrylate oligomer (I) with about 3.0 mol/kg molecule polymerizable double bonds.

[0029] Examples 1 through 4 of radiation-curable adhesive

Example 1

20 weight parts polyester acrylate oligomer (I) was added per 330 weight parts of 30 wt% polyester resin (I) solution, and the resulting solution was adjusted to a solids content of 30 wt% with methyl ethyl ketone, giving adhesive A.

[0030] Example 2

60 weight parts polyester acrylate oligomer (I) was added per 330 weight parts of 30 wt% polyester resin (II) solution, and the resulting solution was adjusted to a solids content of 30 wt% with methyl ethyl ketone, giving adhesive B.

[0031] Example 3

10 weight parts polyester acrylate oligomer (I) and 10 weight parts polyurethane oligomer "Aronix M1200" (Toa Gosei) were added per 330 weight parts of 30 wt% polyester resin (I) solution, and the resulting solution was adjusted to a solids content of 30 wt% with methyl ethyl ketone, giving adhesive C.

[0032] Example 4

A coating material was prepared with adhesive A prepared in Example 1 by dispersing the titanium white pigment JR-300 (by Teikoku Kako) in a pigment/binder ratio of 2. The coating solids were adjusted to 45 wt%, giving adhesive D.

[0033] Examples 5 through 9 of PET laminated metal sheets and their production

Example 5

Adhesive A was applied by a bar coater to a thickness of 3 μm on the corona discharge-treated side of an Ester Espet Film E5100 by Toyobo (12 μ thick PET film treated by corona discharge on one side). The coated film was passed through a drying furnace (120°C × 20 seconds) to allow the solvent to evaporate off, resulting in a tack-free state. The coated PET film and 0.19 mm thick tinplate Canlight (Nippon Steel Corporation) were hot laminated at a rolling pressure of 5.0 kg/cm^2 and a rolling temperature of 180°C. The laminated metal sheet was then irradiated (4 Mrad) through the PET film using an electron beam accelerator at an acceleration voltage of 270 KeV and a current of 50 mA so as to cure the adhesive layer, giving a PET laminated metal sheet. Various performance tests of the resulting PET laminated metal sheet gave the results in Table 1.

[0034]

[Table 1]

	Metal sheet	Adhesive	Coating thickness	Laminating conditions		Radiation conditions			Adhesion	Processing	Retort resistance		Thermal stability
				Rolling pressure (kg/cm^2)	Rolling temp. (°C)	voltage	current	dose	180° peel (g/15 mm)	Dupont impact	Whitening	Adhesion	
Example 5	tinplate	A	3 μ	5	180	270	50	4	500	good	good	good	good
Example 6	tinplate	B	2 μ	5	180	250	40	3	450	good	good	good	good
Example 7	tinplate	C	3 μ	5	180	250	40	3	550	good	good	good	good
Example 8	tinplate	D	4 μ	8	180	270	50	4	400	good	good	good	good
Example 9	tin-free steel	A	3 μ	5	180	270	50	4	500	good	good	good	good
Compar. Ex. 1	tinplate	Compar. 1	3 μ	5	180	--	--	--	350	good	whitened	10% separation	good

[0035] Examples 6 through 9

PET laminated metal sheets were obtained in the same manner as in Example 5 under the conditions in Table 1. The results of performance tests are given in Table 1. The following tests were performed.

[0036] (1) 180°C Peel test: based on JIS K-6744

[0037] (2) Dupont impact test: The surface of the PET film was struck (1/2 inch, 500 g load, 50 cm height), and the sheets were checked for any separation between the metal sheet and PET film.

[0038] (3) Retort resistance

Coatings exposed to tap water steam in an autoclave (1.4 atm pressure, 125°C × 30 min) were checked for whitening and checkboard adhesion.

[0039] (4) Thermal stability

Laminated sheets were cut to dimensions of 5 cm × 5 cm and heat treated for 2 minutes at 200°C, and the PET films were checked for heat shrinkage.

[0040] Comparative Example 1

PET laminated metal sheets were obtained in the same manner as in Example 5 using an adhesive (Comparison 1) which had been obtained by adding blocked tolylene diisocyanate as a curing agent to 300 weight parts of the polyester resin (I) solution obtained in Production Example 1 instead of the adhesive A used in Example 1. The results of performance tests are given in Table 1.

[0041]

[Effect of the Invention]

The PET laminated metal sheets obtained in the present invention have better adhesion between the PET film and metal material, as well as better retort resistance when used on food product cans. Furthermore, the use of a polyester resin radiation-curable adhesive to laminate PET films and metal materials allows the adhesive curing process to be completed far more rapidly during production, while also saving plant space. The lower energy consumption is also more economical.